











# NAVAL POSTGRADUATE SCHOOL

## Monterey , California



## THESIS

D1413

Interface Characterization of Cu-Cu and  
Cu-Ag-Cu Low Temperature Solid State Bonds .

By

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1 1 0

December 1987

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T238797



## REPORT DOCUMENTATION PAGE

1a REPORT SECURITY CLASSIFICATION <b>UNCLASSIFIED</b>			1b RESTRICTIVE MARKINGS		
2a SECURITY CLASSIFICATION AUTHORITY			3 DISTRIBUTION / AVAILABILITY OF REPORT Approved for public release; distribution is unlimited.		
2b DECLASSIFICATION / DOWNGRADING SCHEDULE			5 MONITORING ORGANIZATION REPORT NUMBER(S)		
4 PERFORMING ORGANIZATION REPORT NUMBER(S)			5 MONITORING ORGANIZATION REPORT NUMBER(S)		
6a NAME OF PERFORMING ORGANIZATION  Naval Postgraduate School		6b OFFICE SYMBOL (If applicable)  69		7a NAME OF MONITORING ORGANIZATION  Naval Postgraduate School	
6c ADDRESS (City, State, and ZIP Code)  Monterey, California 93943-5000			7b ADDRESS (City, State, and ZIP Code)  Monterey, California 93943-5000		
8a NAME OF FUNDING / SPONSORING ORGANIZATION		8b OFFICE SYMBOL (If applicable)		9 PROCUREMENT INSTRUMENT IDENTIFICATION NUMBER	
8c ADDRESS (City, State, and ZIP Code)			10 SOURCE OF FUNDING NUMBERS		
			PROGRAM ELEMENT NO	PROJECT NO	TASK NO
			WORK UNIT ACCESSION NO		
11 TITLE (Include Security Classification) <b>INTERFACE CHARACTERIZATION OF Cu-Cu AND Cu-Ag-Cu LOW TEMPERATURE SOLID STATE BONDS</b>					
12 PERSONAL AUTHOR(S) <b>Dalbey, Robert Z.</b>					
13a TYPE OF REPORT <b>Masters Thesis</b>		13b TIME COVERED FROM _____ TO _____		14 DATE OF REPORT (Year, Month, Day) <b>1987, December</b>	
15 PAGE COUNT <b>53</b>					
16 SUPPLEMENTARY NOTATION					
17 COSATI CODES			18 SUBJECT TERMS (Continue on reverse if necessary and identify by block number)		
FIELD	GROUP	SUB-GROUP	Interface Characterization, Auger Spectroscopy, Solid State Bonding, Diffusion Bonding, Scanning Electron Microscopy		
19 ABSTRACT (Continue on reverse if necessary and identify by block number) In this study, Auger Electron Spectroscopy (AES), Scanning Electron Microscopy (SEM) and Energy Dispersive X-ray (EDX) analysis have been used to characterize the interface regions of copper to silver and copper to copper bond samples in an effort to identify those parameters which most affect the bond characteristics. Longitudinal and transverse cross sections of the bond joint are examined. Auger electron sputter depth profiling was used to examine the interface properties and composition across the bond interface. Depth profiles indicate carbon and oxygen diffuse away from the interface during bonding facilitating adhesion. Tensile tests on bonded samples indicate that bond pressure has a more significant effect on bond strength than temperature. A temperature threshold for bonding is observed which is related to the ability of the bond materials to scavenge their oxides. The difference in bond					
20 DISTRIBUTION / AVAILABILITY OF ABSTRACT <input checked="" type="checkbox"/> UNCLASSIFIED/UNLIMITED <input type="checkbox"/> SAME AS RPT <input type="checkbox"/> DTIC USERS			21 ABSTRACT SECURITY CLASSIFICATION <b>UNCLASSIFIED</b>		
22a NAME OF RESPONSIBLE INDIVIDUAL <b>K. D. Challenger</b>			22b TELEPHONE (Include Area Code) <b>(408) 646-3036</b>		22c OFFICE SYMBOL <b>69CH</b>

19.

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Interface Characteristics of Cu-Cu and  
Cu-Ag-Cu Low Temperature Solid State Bonds

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Submitted in partial fulfillment of the  
requirements for the degree of

MASTER OF SCIENCE IN ENGINEERING SCIENCE

from the

NAVAL POSTGRADUATE SCHOOL  
December 1987

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Thesis  
D1413  
C.1

## ABSTRACT

In this study, Auger Electron Spectroscopy (AES), Scanning Electron Microscopy (SEM) and Energy Dispersive X-ray (EDX) analysis have been used to characterize the interface regions of copper to silver and copper to copper bond samples in an effort to identify those parameters which most affect the bond characteristics. Longitudinal and transverse cross sections of the bond joint are examined. Auger electron sputter depth profiling was used to examine the interface properties and composition across the bond interface. Depth profiles indicate carbon and oxygen diffuse away from the interface during bonding facilitating adhesion. Tensile tests on bonded samples indicate that bond pressure has a more significant effect on bond strength than temperature. A temperature threshold for bonding is observed which is related to the ability of the bond materials to scavenge their oxides. The difference in bond strength/toughness for Cu-Cu bonds versus Cu-Ag-Cu bonds may qualitatively indicate the magnitude of the chemical energy term associated with joining these two dissimilar metals.

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## I. INTRODUCTION

Diffusion bonding is a joining technique which produces a metallurgical bond between materials without the formation of a liquid phase. The technique was used as long ago as the middle ages to produce tools which required a hardened edge. The high cost and limited availability of steel billets large enough for entire component fabrication forced early blacksmiths to bond steel to softer metals for those tools which required a hardenable edge. Swords were later made by hammer welding strips of carburized steel lengthwise to form a blade with a more uniform carbon distribution than could be obtained by carburizing the completed blade. These processes typically required the heating of components to white hot temperatures, possibly fluxing with sand, and hammering the components together to get the surfaces close enough for bonds to form.

As crude as these techniques appear today, they contain the essential requirements for solid state bonding as currently understood. That is, they forced the two surfaces close enough together for atomic bonds to form across the interface and they provided thermal activation for the diffusion process. Anything which might inhibit either of the above should have a deleterious effect on the bond formed.



Development of techniques today is driven by the need for low temperature joining methods suitable for a variety of new materials which would suffer significant degradation of mechanical properties if subjected to the thermal cycle associated with more common joining practices. These low temperatures are insufficient to activate most bulk diffusion modes and therefore, impose new, stringent requirements on the surface conditions of the components to be joined.

For bonding, atoms must be forced close enough together, typically three to five angstroms, to form a stable metallic bond with a significant lifetime. Outer shell electron interactions may occur over much larger atomic distances if atoms are in an excited state (i.e. electrically, thermally, optically, etc.) but probably contribute very little to bonding in the current context. Obviously oxides and adsorbed contaminants may act as barriers which prevent atoms from approaching close enough for metal-metal bonds to form. In some cases oxygen does not prevent bonding, e.g. chromium bonding with  $\text{Cr}_2\text{O}_3$  on 300 series stainless, but the inclusion of brittle oxides at the interface can adversely affect bond ductility. Fusion welding is less affected by the presence of these contaminants in most cases because the molten weld pool can carry them away from the solid liquid interface and diffuse them dynamically within the weld pool.

High temperature diffusion welding processes are also somewhat less affected by the presence of surface contaminants because the material may be heated to the point where significant plastic deformation can be achieved. Oxides and other surface contaminants are either extruded from the interface where joining is desired, or diffused into the bulk material and diluted to such an extent that they no longer inhibit joining.

Low temperature bonding ( $0.3 T_m$  to  $0.5 T_m$ ) does not inherently possess the ability to restructure the surfaces of components being joined. It has become apparent that the successful application of low temperature bonding techniques will require a fuller understanding of the mechanisms responsible for metallic bonding across the interface.

This research examines the interfaces of bond specimens produced by an RF-induction heated bonding apparatus described in an earlier thesis [Ref. 1]. The emphasis in the present study is on bonding mechanisms and attempts to identify those mechanisms which are most critical to the formation of a satisfactory bond.

## II. BACKGROUND

Solid state bonding has been the subject of increasing experimental investigation, primarily since the early 1960's. The field still lacks a single comprehensive theory describing bond formation across the interface, however.

In fusion welding the joint is formed via alloying and resolidification from the liquid state. In this case it is possible to metallographically define the bond mechanism as the metallurgical and crystallographic extension of a modified parent phase into a new daughter phase. The transition from parent to daughter phases may occur over a few tenths of a millimeter to several centimeters, i.e. several million lattice units. The solid state bond in theory is infinitely abrupt, involving only those atoms associated with the two mating surfaces. In reality the solid state bond involves nonideal surfaces and effects such as local deformation, diffusion and surface reconstruction and the bond region may extend approximately 100 lattice units.

At temperatures above half the absolute melting temperature ( $T > 0.5 T_m$ ) of the lowest melting point parent material, bulk diffusion may take on a major role in the solid state bond process. At these higher temperatures the condition of the surfaces to be joined is less critical

because surface contaminants can diffuse away from the interface allowing intimate contact between the metals to be joined. Interdiffusion, grain growth and grain boundary migration are possible at temperatures greater than half the melting temperature and each of these may affect the resulting bond. Intermetallic phases have been observed in solid state bonding processes involving pure elements at higher temperatures indicating the extent to which interdiffusion may occur [Ref. 2]. Such high temperature bonding processes are therefore referred to as diffusion bonding and like fusion welding are characterized by metallurgical and crystallographic transitions from the parent to daughter phases.

As temperatures are reduced ( $T < 0.5 T_m$ ), the role of diffusion in bond formation diminishes due to the reduction of thermal energy available for activation. At room temperature, bulk diffusion is negligible in the tungsten/platinum system but single metal point to metal foil bonds with significant strength have been produced in vacuum [Ref. 3] suggesting that diffusion may not be a requirement for bond formation. The term pressure bonding has been applied to joints formed under those conditions in which temperatures are kept low and the addition of heat to the system is minimized.

In fact, as will be shown later, theoretically there may exist sufficient cohesive energy for bond formation to



occur at absolute zero if the surfaces are close enough for bond reactions to proceed. Of prime importance then is the ability to bring the surfaces to be joined into close enough proximity for atomic interaction between them.

If two perfect surfaces, atomically clean and atomically flat, could be brought together a bond should form. This can be shown by considering a simple energy expression. Let;

$${}^1E_B {}^1V_B + {}^1E_S {}^1A_S + {}^2E_B {}^2V_B + {}^2E_S {}^2A_S = E_{(1+2)} \quad (1)$$

be the total volume and surface energies of two separate metal systems, 1 and 2. The  ${}^iE_B$ 's represent bulk free energies per unit volume of the respective systems and the terms,  ${}^iE_S$ , represent the surface free energies per unit area.  ${}^iV_B$  and  ${}^iA_S$  are the respective bulk volumes and surface areas. Upon placing the two systems in contact some of the surface energy associated with the previous system is lost or given up and is presumably available for bonding. As shown below the two systems in contact represent a lower energy state and therefore bonding or joining should be favored. Here  $A_C$  represents the true area of contact

$$E_{(1+2)} - A_C({}^1E_S + {}^2E_S) < E_{(1+2)} \quad (2)$$

between the surfaces, that is the true area over which atoms from one surface experience the repulsive force of atoms associated with the other surface. If two dissimilar metals are to be joined an additional positive interface energy

term must be considered (Equation 3). Here the interface energy per unit area is indicated as  $E_I$ . As long as the total energy of the two systems in contact is lower than the energy of the two separate systems bonding is favored. This assumption highlights the importance of the interface energy term. The physical origin of this term and its evaluation will be discussed further later in this paper.

$$E_{(1+2)} - A_C(^1E_S + ^2E_S) + A_C E_I = E_{TOTAL} \quad (3)$$

Perfect surfaces are an abstraction, however, and provide little insight into the processes important in engineering applications of solid state bonding. True surfaces are neither atomically clean nor flat. Even the best surfaces are rough on an atomic scale and they carry considerable contaminants. Surface roughness reduces the true area of contact between two surfaces. The reduced area of contact limits the amount of energy made available for bonding via the elimination of surface area.

True contact area is the fractional portion of the total geometric area for which atoms associated with one or the other parent surfaces experiences the repulsive field of atoms on the other surface. Efforts to arrive at estimates of total contact area through the use of analytical models are plagued by the complex interaction of elastic and plastic strain. In small structures (asperities), for example, minute portions of single crystals may resist plastic deformation by loads an order of magnitude larger

than those required to deform the bulk [Ref. 4]. Analytical models also assume a rough deformable surface in contact with a smooth nondeformable surface. This later simplification is adequate when considering the bonding of a soft material to a very hard material (e.g. aluminum to steel) but is quite removed from the actual processes involved in the bonding of two soft materials, like copper to silver, in which case both materials plastically flow at high loads.

Experimental efforts to determine contact area also suffer from substantial limitations. Attempts to measure resistance across an interface are questionable because of electron tunneling across gaps of approximately 10 angstroms or the presence of thin oxide layers which reduce conduction across the interface.[Ref. 4]

Ultrasonic methods which measure the acoustic energy transmitted through an interface have also been used in an attempt to evaluate contact area. In this case the energy transmitted through a small constriction is proportional to the diameter of the constriction. Quantitative evaluation of the data, then, requires a priori knowledge of the number of contact points and the statistical distribution of their sizes. The number of contact points and their size distribution is typically estimated from surface profilometry studies but may be in error by as much as one

or two orders of magnitude due to local variations in surface topography not detected by the profilometer.

[Ref. 4]

Surface analytical techniques are approaching the resolution required to map the effects of contact at the interface (Tunneling Electron Microscopy, Ion Microprobe, etc.) and thus provide an accurate evaluation of true contact area. From an engineering or process point of view use of these techniques requires separation of the joined components, i.e. destructive testing. The results are also biased by the final surface structure where fracture topography and fracture path will profoundly affect the data collected.

Surface contaminants can also impede the bond strength of a couple by preventing the surface to be joined from approaching close enough for the desired bond mechanism to become operative. Common surface contaminants are oxides, sulfides and hydrocarbons, all of which typically occur upon atmospheric exposure. Two choices for bond processing become immediately apparent. Remove those steps which involve atmospheric exposure and/or choose those materials which are less reactive upon atmospheric exposure. Those approaches which combine both have been most successful [Ref. 5, 6, 7, 8]. The research efforts presented here were confined to examining materials which exhibit minimal reactivity upon atmospheric exposure.



It is the valence electrons which are primarily responsible for the bonding of materials because these electrons occupy a lower energy state in the solid than they do in the free atom. If  $\Phi$  represents the wave function of a valence electron for a free atom,  $\Phi$  is observed to oscillate in the vicinity of the nucleus then decay exponentially to zero at some distance removed from the nucleus. Wave functions for s electrons are particularly simple because they are spherically symmetric and such functions for s electrons in multi-electron atoms may be closely modeled by the wave function for an s electron in a single electron atom (H). The wave function for the 4s electron of copper is shown in Figure 1 for two atoms in close proximity.

When a number of atoms are brought together to form a solid, the valence electron wave functions are modified such that they connect smoothly with the wave function of nearest neighbors at the boundary of the Weigner-Seitz cell. The requirement for continuity at the cell boundary prevents the wave function from approaching zero reducing the curvature of the function in the vicinity of the cell boundary (see Figure 1). The kinetic energy of the electron represented by  $\Phi$  is proportional to  $-\nabla^2\Phi$ , that is, the kinetic energy of the electron is proportional to the second derivative or curvature of  $\Phi$  [Ref. 9]. The energy of the electrons in the bound atom are therefore lower than the energy of electrons

associated with a free atom as indicated by the reduced curvature of  $\Phi$ . The potential energy of the system is also lower because valence electrons in the solid are confined to regions closer to the nucleus. (The potential energy varies inversely with electron distance from the nucleus,  $V \propto 1/r$ .) The reduction of kinetic and potential energy in the solid state is the source of cohesive energy which binds atoms together.

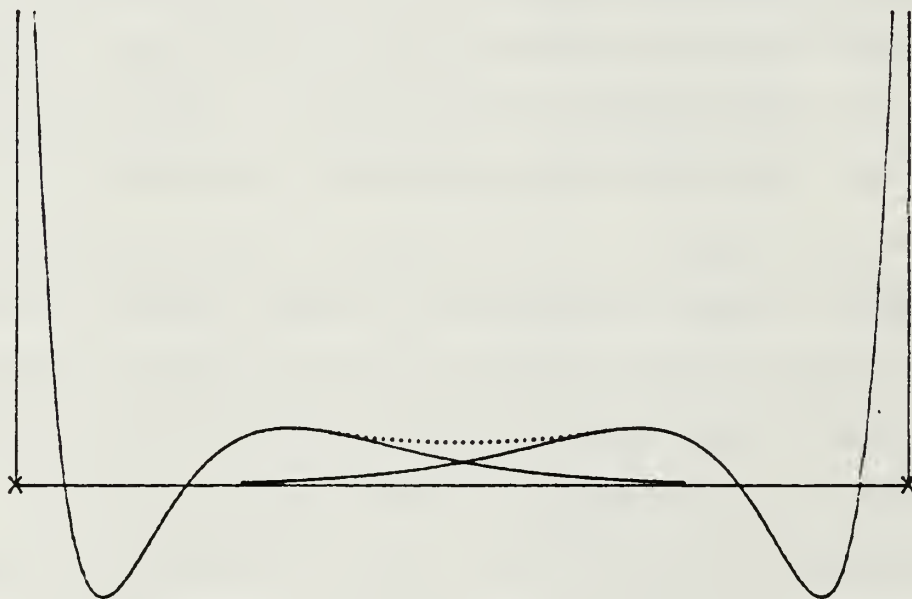


Figure 1.  
The Wave Functions For 4s Electrons In Cu.  
The dotted line indicates modification of  
wave function in a 1 dimensional solid.

There is a positive energy contribution associated with the bound state. Valence atoms in solid copper are not confined to specific energies but exist within a broad band.

Translational kinetic energy within the band reduces the cohesive energy.

The cohesive energy, the energy binding the atom to the solid may now be approximated by the following formulas.

$$E_{\text{FREE ATOM}} - E_{\text{BOUND ATOM}} = E_{\text{COHESIVE}} \quad (4)$$

$$E_{\text{COHESIVE}} = -\Delta E_{\text{KINETIC}} - \Delta E_{\text{POTENTIAL}} + E_{\text{TRANSLATION}} \quad (5)$$

If two dissimilar elements bond together or alloy with one another, continuity of the wave function at cell boundaries is still required. If the wave functions for valence electrons are significantly different, it is expected that one or both parent wave functions will have to change curvature considerably to achieve continuity. In this case the modification of curvature represents a positive energy contribution opposing bond formation and is the source of the interface energy term in Equation 3. A change in the amplitude of the wave function also reflects a change in the electron density. Thus if two dissimilar metals form a bond, continuity of the wave function across the cell boundary or interface may require charge transfer from one atom to another.

A. R. Miedema, et al., using a thermodynamic approach have related the enthalpy of formation for a binary alloy to the difference in work functions of the two metals and the difference in electron density for the specific atoms at the boundaries of the Weigner-Seitz cell. The relation for the

enthalpy was derived from experimental data on the heat of mixing liquid metals and determined to be [Ref. 10-13]:

$$\Delta H \simeq [-P_0 e (\Delta\phi')^2 + Q_0 (\Delta n_{ws}^{1/3})^2 - R] \quad (6)$$

The above equation is only qualitative in that it predicts only the sign of the enthalpy of formation for a specific alloy. Negative values predict mixing or alloying, positive values predict no tendency to alloy. The quantity  $e$  refers to the elementary charge of an electron.  $P$  and  $Q$  in Equation 6 are variables used to fine tune the prediction and are experimentally determined by examining phase diagrams to determine if alloying occurs.  $R$  is a term which represents the additional energy associated with p-d hybridization found in some systems and is nonzero only for combinations of a d transition element with a p transition element. The term  $\Delta\phi'$  refers to the difference in the work function between the two base materials and  $\Delta n_{ws}$  is related to the change in electron density at the cell boundary associated with bond formation in the alloy. In Equation 6  $\Delta\phi'$  is a slightly modified value of the difference in work functions for the two pure elements considered and can be related to an electrostatic binding term due to charge transfer from one atom to another.

Attempts at estimates of  $\Delta n_{ws}$  require summing the contributions of electron wave functions for all valence electrons at the cell boundary. For the case of copper and



silver, summations over both s and d electron contributions are required. Such evaluations are quite difficult for all but the simpler metals and are seldom as accurate as desired. For example, in the case presented for copper so far only the wave function for the s electron has been considered, but it is known that the underlying 3d electrons also take part in bond formation. The d electron wave function is not spherically symmetric suggesting directional preference for bonding. In fact this has been observed [Ref. 14].

Due to the difficulty of an analytical approach to the determination of  $\Delta n_{ws}$ , Miedema showed that this term could be related empirically to the compressibility of the pure metal. It was shown that  $\Delta n_{ws}$  may be reasonably approximated by  $(B/V_m)$  where B is the bulk modulus and  $V_m$  is the molar volume. [Ref. 10]

The theory developed by Miedema et al. has been applied by Oberg et al. to the prediction of stability of explosive welds, another solid state bond process. These authors found that a slightly positive chemical energy term prevented the formation of intermetallics. As long as the positive chemical energy was less than the energy reduction due to the elimination of surface area, a stable bond was predicted. [Ref. 15]

The lack of an intermetallic is suggested by the binary phase diagram for copper and silver but the magnitude of the

chemical energy term is not apparent from the diagram. Based on Oberg's analysis copper and silver are excellent candidates for solid state bonding without the formation of an embrittling intermetallic because the chemical energy term is small enough not to interfere with bonding.

Assuming the enthalpy term derived by Miedema represented a chemical potential for alloying, the term was rescaled to reflect the contact surface of a macroscopic interface vice the surface area of one face of the Weigner-Seitz cell. This surface chemical potential relates only to two atomically clean surface and like the enthalpy term expressed in Equation 6 may be either positive or negative. The two mating surfaces in contact are further assumed to approximate a high angle grain boundary and the energy associated with this new grain boundary is assumed to be 0.3 times the average surface energies of the two materials. The sum of the surface chemical potential and the high angle grain boundary energy is equivalent to the interface energy term,  $E_I$ , used in Equation 3. The surface

$$E_I = 0.3 * (^1E_S + ^2E_S) / 2 + E_{Chem} \quad (7)$$

chemical potential based on Miedema's theory is represented as  $E_{Chem}$  in Equation 7.

The bond energy is then the difference between the initial total energy of the two separate systems and the final energy of the bonded system. Referring to Equation 3

this may be expressed in the following way.

$$E_{\text{TOTAL}} - E_{(1+2)} = -A_C(^1E_S + ^2E_S) + A_C E_I \quad (8)$$

Substituting for  $E_I$  from Equation 7 yields the following expression:

$$E_{\text{TOTAL}} - E_{(1+2)} = -.85A_C(^1E_S + ^2E_S) + A_C E_{\text{Chem}} \quad (9)$$

This equation clearly shows that  $E_{\text{Chem}}$  can be positive, indicating a tendency not to form intermetallic compounds, but stable bonds are still possible as long as this term is less than  $.85(^1E_S + ^2E_S)$ .

If  $E_I$  (Equation 7), the interface energy of the couple is plotted versus surface energy of the partner metal  $^2E_S$  for each metal couple considered for bonding, a scatter diagram is generated. A horizontal line can be drawn through the scatter diagram at  $0.3 \cdot ^1E_S$  (line 1 in Figure 2) representing the interface energy term associated with a similar metal bond (for example Ag-Ag which exhibits only the grain boundary energy term). Another sloping line is drawn at  $0.3 \cdot ^xE_S$  over the range of surface energies (line 2 in Figure 2) corresponding to those couples considered for bonding (this line represents the grain boundary interface energy term for the second metal). A bisecting line can also be drawn between the two corresponding to high angle grain boundary energy term for a couple composed of metal 1 and any other metal x (line 3 in Figure 2). The points plotted in the diagram may now be evaluated based on their relative positions to these lines.

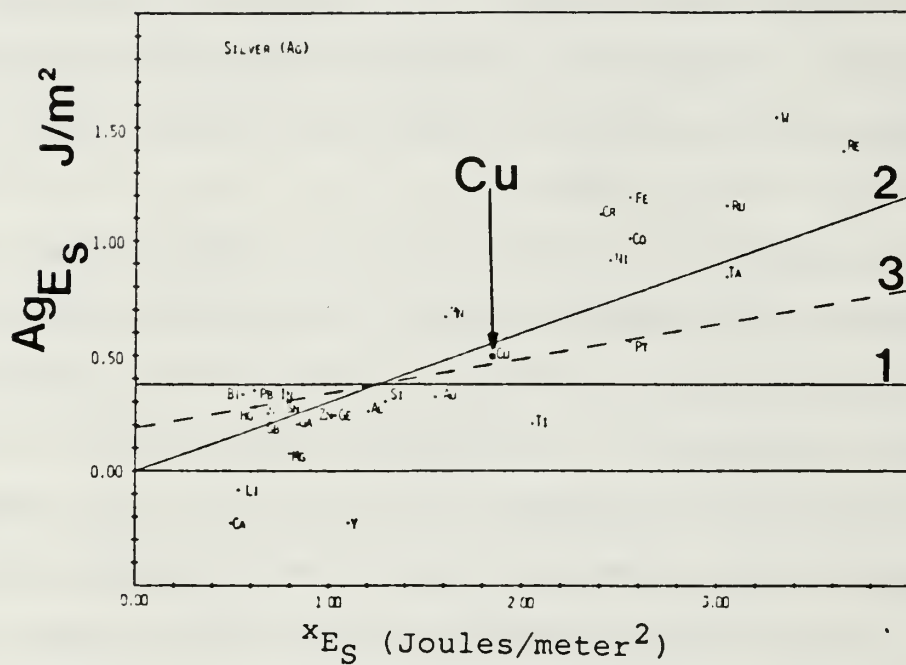


Figure 2  
Bond Interface Energy Versus Surface Energy of  
Element X [Ref. 15]

Those points which lie below the  $0.3 \cdot ({}^1E_S + {}^xE_S)/2$  line represent metals which exhibit a negative chemical energy (favors bonding). Points near this line indicate metals whose interface energy is primarily due to the grain boundary energy term and for which the chemical energy term based on Miedema's theory is small. Points above this line indicate high chemical energy terms. Points slightly above the line are metals with slightly positive chemical energy terms which should resist the formation of intermetallics.

Figure 2 is a graph for the silver-x-metal [Ref. 15] system which suggests copper and silver should form satisfactory solid state bonds. It can be seen from the graph that the Ag-Cu couple has a slight positive chemical energy which should resist intermetallic formation but is small enough that its effect on bond formation should be minimal. The phase diagram for the copper silver system also indicates that no intermetallic is expected but the phase diagram does not provide the qualitative insight into the bondability of the two metals.



### III. EXPERIMENTAL

The apparatus used for the investigation of low temperature bonding has been described elsewhere [Ref. 1]. Bond specimens are inductively heated and forced together at the desired bond pressure by a hydraulic ram. Photographs of the current bonding system are shown in Figure 3.



Figure 3

#### The Diffusion Bonding System

Full bonding system on left. Ram, heater coil and tensile specimen on right. [Ref. 1]

Because the ability of the system to produce low temperature bonds has been demonstrated, the thrust of this effort was to examine bond characteristics as a function of

time, temperature and pressure. The number and type of samples used in this effort are more varied than those used in the previous effort [Ref. 1].

Preliminary work focused on the bonding of pure metal foils, copper (Cu) and silver (Ag). The bonding of foils allowed rapid feedback regarding the character of the bond interface without the requirement of vacuum coating test specimens. Foils also allowed additional flexibility in designing the bonds to be investigated, i.e. Cu-Cu, Cu-Ag, Ag-Ag and Cu-Ag-Cu.

The use of copper and silver facilitated the investigation of low temperature dissimilar metal bonds. Efforts reported previously [Ref. 16,17] dealt with the use of intermediate materials at the bond interface where the interlayer material was vacuum deposited on the surfaces to be bonded. Actual deposition processes have included hot hollow cathode, vacuum evaporation, electroplating and RF-sputter deposition [Ref. 18, 19, 20]. Subsequent testing of these specimens dealt primarily with the integrity of the single interlayer/interlayer interface by subjecting bonded samples to tensile loads sufficient to cause failure. The resultant fracture path was then used to evaluate the bond which had been formed.

In the present study, 500 micron thick copper foil and 25 micron thick silver foil were used to determine the

critical parameters for bond formation. The copper foil was initially deoxidized by swabbing with dilute hydrochloric acid (HCl). One face of the foil was then hand polished to a mirror finish using first 15 micron diamond polish followed by 3 micron and 1 micron polishes. Thick napped polishing cloth was used to apply the diamond polish. The foil was ultrasonically rinsed in water after polishing. Some light scratches were still visible to the naked eye after polishing. No surface preparation other than deoxidizing with dilute HCl was performed on the silver foil due to its fragile nature. Foils were bonded immediately after cleaning.

Tensile test specimens used in the previous effort [Ref. 1] were used as the bonding rams in this investigation (Figure 4). The test specimens were parted in the middle and faced to produce a relatively smooth surface. The tensile specimens were then surface ground by hand in a manner similar to that used to produce telescope lenses. Forty five micron diamond polish was applied to the mating surfaces of the tensile specimen and the faces were rubbed together in a circular fashion. When machining marks were no longer visible, the polish was reduced to 15 micron followed by 3 and 1 micron polish. This procedure provided flat parallel faces which produced even bonding pressure across the entire bond area (0.2 square inches, 1.3 square centimeters).

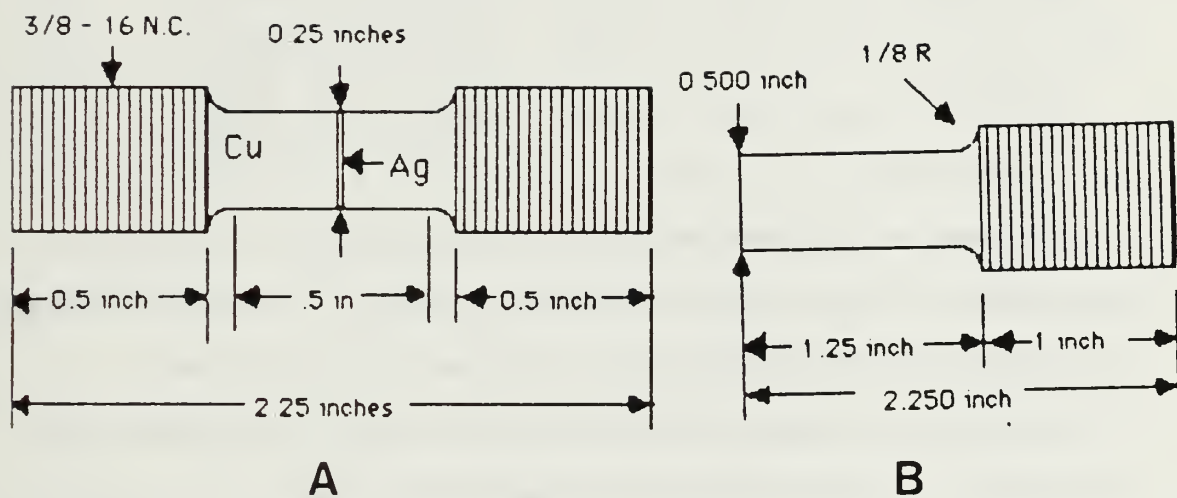


Figure 4  
Tensile Test Specimen (A) and Bonding Ram (B)

The test matrix outlined in Table 1 was followed during the course of preliminary testing. The matrix was chosen to follow the work presented by Dini, et al. [Ref. 20]

TABLE 1  
BOND PARAMETER MATRIX USED IN FOIL BONDING TESTS.

<u>MATERIAL BONDED</u>	<u>BOND PRESSURE</u>	<u>BOND TEMPERATURE</u>	<u>TIME Hr.</u>
Cu/Cu	20 KSI (138 MPa)	423K (0.31 T <sub>m</sub> Cu)	0.5,1
		473K (0.34 T <sub>m</sub> Cu)	0.5
		523K (0.39 T <sub>m</sub> Cu)	0.5
Cu/Ag/Cu	20 KSI (138 MPa)	423K (0.34 T <sub>m</sub> Ag)	0.5,1
		473K (0.38 T <sub>m</sub> Ag)	0.5
		523K (0.42 T <sub>m</sub> Ag)	0.5
Cu/Ag/Cu	25 KSI (173 MPa)	423K (0.34 T <sub>m</sub> Ag)	0.5,1
		473K (0.38 T <sub>m</sub> Ag)	0.5

Bonded foils were subsequently sectioned to provide specimens for interface characterization. Transverse cross sections were prepared using standard metallurgical techniques and then examined in the optical microscope to determine if gross delaminations were present. The samples were then transferred to a scanning electron microscope (SEM) or a scanning auger microprobe (SAM) for detailed investigation of interface regions. Elemental line scans and maps were used to determine the extent of reactions occurring at the interface.

Bonded foils were also low angle lapped and polished (3-8 degrees) so that auger depth profiling could be used to further examine the interface region. Depth profiling was performed using 1KV argon ions at approximately 40 degree



angle of incidence. Profile data was collected by alternately sputtering then acquiring auger peak amplitudes for the elements monitored, typically copper, silver, oxygen and carbon. The profiles of some samples were suspended at times of particular interest and general surveys were taken to assure that other elements which might affect bond characteristics had not been introduced to the experiment.

Based on the ability to produce bonds in foils, copper bond specimens were machined which could be screwed into modified tensile specimens which acted as rams during the bond process. These bond specimens were similar to the larger specimens used as bonding rams but scaled down in size. Figure 4 shows the specimen geometry for both ram and copper tensile specimen. Copper tensile specimen dimensions are in parenthesis. Machined copper bond specimens were then subjected to the same surface treatment utilized to prepare the rams for bonding the foils, again to insure smooth flat mating surfaces. Just prior to bonding, the copper blanks were cleaned in dilute HCl and rinsed in water. The blanks then received a light 1 micron polish followed by an water/methanol/water rinse cycle and blown dry.

After bonding, specimens were pulled to failure using modified tensile specimen blanks as grips for the tests. Tensile tests provided data regarding the integrity of the

bond. SEM and energy dispersive X-ray analysis were performed on the fracture surface to determine fracture mode and path.

All bonds formed using the machined copper samples were Cu/Cu or Cu/Ag/Cu bonds. Bonding parameters were similar to those listed in Table 1 for the foils bonded to allow correlation between interface analysis and measured bond strength.

#### IV. RESULTS AND DISCUSSION

A summary of results for various bond tests of foils and tensile specimens is presented in Table 2. Those samples which bonded are indicated with a "B" and samples which failed to bond are indicated by "NB". "XXXX" indicates those conditions for which bonds have not been attempted.

TABLE 2  
BOND RESULTS FOR VARIOUS TEST CONDITIONS

		<u>FOILS</u>		<u>TENSILE</u>	
		<u>0.5Hr</u>	<u>1Hr</u>	<u>TEMP.</u>	<u>0.5Hr</u> <u>1Hr</u>
<u>Cu-Cu</u>	20ksi	B	B	150C	NB   XXXXX
		B	XXXXX	200C	B   XXXXX
		B <sub>1</sub>	XXXXX	250C	B   XXXXX
<u>Cu-Ag-Cu</u>	20ksi	B	B	150C	XXXXX   XXXXX
		B	XXXXX	200C	B   XXXXX
		XXXXX	XXXXX	250C	B   XXXXX
<u>Cu-Ag-Cu</u>	25ksi	B	B	150C	XXXXX   B
		B <sub>1</sub>	XXXXX	200C	XXXXX   B
		XXXXX	XXXXX	250C	XXXXX   XXXXX

A 1 indicates the aluminum ram plastically deformed during the test. A 2 indicates the test was not run for the full time indicated.

All foil systems bonded at all temperatures and loads used. Foil bonds were subsequently cut into thirds for further evaluation. All foils survived the cutting procedure but the 150C 20ksi bonds failed at some point during latter processing indicating a weaker bond was formed

under these conditions. A metallographic cross section for a Cu-Cu bond specimen is presented in Figure 5. The etch reveals the grain boundary like nature of the interface and shows clearly that no grain growth or grain boundary migration has occurred across the interface.



Figure 5  
Light Micrograph Of Etched Cu-Cu Interface

The only bond failure noted for the tensile specimens occurred at the 150C 20ksi bonding condition. This is not surprising given the poor results for foil bonds generated under the same conditions. In the current bond apparatus, samples are joined in the horizontal position. During the unloading process when the ram recedes the bonded tensile specimen experiences a slight bending moment. This bending moment may have caused the failure of this sample if bonding did indeed occur. These Results suggest that the 150C

temperature is below some critical threshold required for bonding at 20ksi.

Tensile bond specimens were filed, sanded and polished to remove all surface stress concentrations prior to testing. A finished tensile specimen (Cu-Ag-Cu 20ksi, 250C, 30 minutes) is shown in Figure 6. Vertical black lines indicate the location of the interface. The length of the reduced sections were approximately 0.5 inches with diameters varying from 0.217 inches to 0.243 inches.

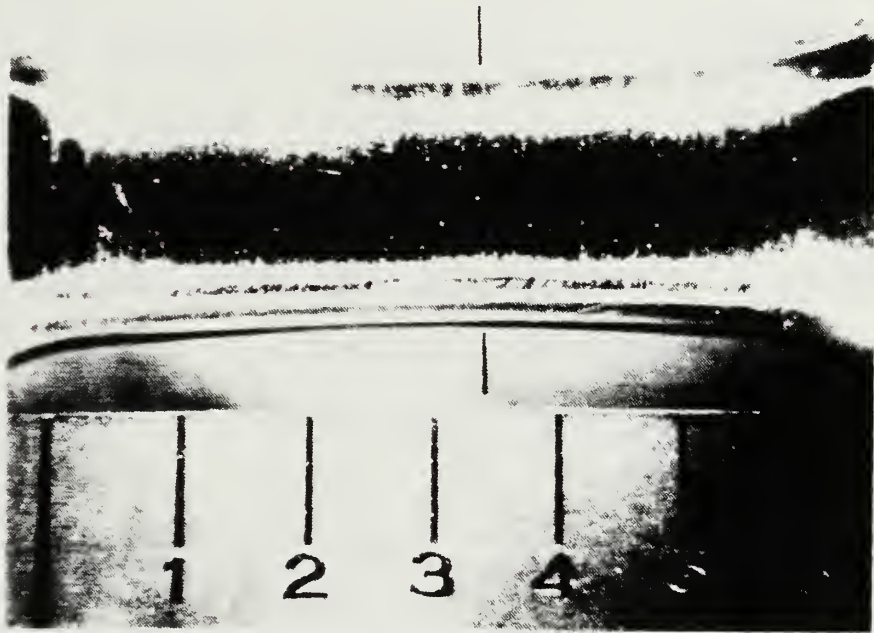


Figure 6  
Bonded Cu-Ag-Cu Tensile Test Specimen

Of the seven tensile specimens attempted, five specimens were available for test. The 25ksi, 150C, 60 minute copper-silver-copper bond tensile specimen failed during mounting for the tensile test. Five specimens were



pulled to failure. Three of the samples exhibited plastic deformation and showed necking prior to failure. Two samples failed in the elastic region before plastic deformation and the onset of necking. Table 3 lists the results of the tensile tests along with the associated bonding parameters. Actual test results for the three

TABLE 3  
RESULTS OF TENSILE TESTS

Bond Pressure-Temp.-Time	Bond System	Max Stress	Elastic or Plastic Region
20-250-30	Cu-Cu	42657psi	Plastic
20-250-30	Cu-Ag-Cu	36511psi	Plastic
25-200-60	Cu-Ag-Cu	43921psi	Plastic
20-200-30	Cu-Ag-Cu	36357psi	Elastic
20-200-30	Cu-Cu	3550psi	Elastic

systems which failed after plastic deformation are presented in Figure 7. During testing a crack was observed on all tensile specimens which subsequently failed after plastic deformation and necking. The presence of the crack near the interface indicates the load carrying cross section was substantially less than that which was measured by the radial extensometer. The crack always extended from one edge towards the center and was not circumferential. The crack, once detected, did not appear to grow in length but continued to widen for the duration of the test.

Scanning electron micrographs clearly show the ductile nature of the failure surfaces (Figures 8,9,10). Auger and energy dispersive X-ray analysis indicate that failure

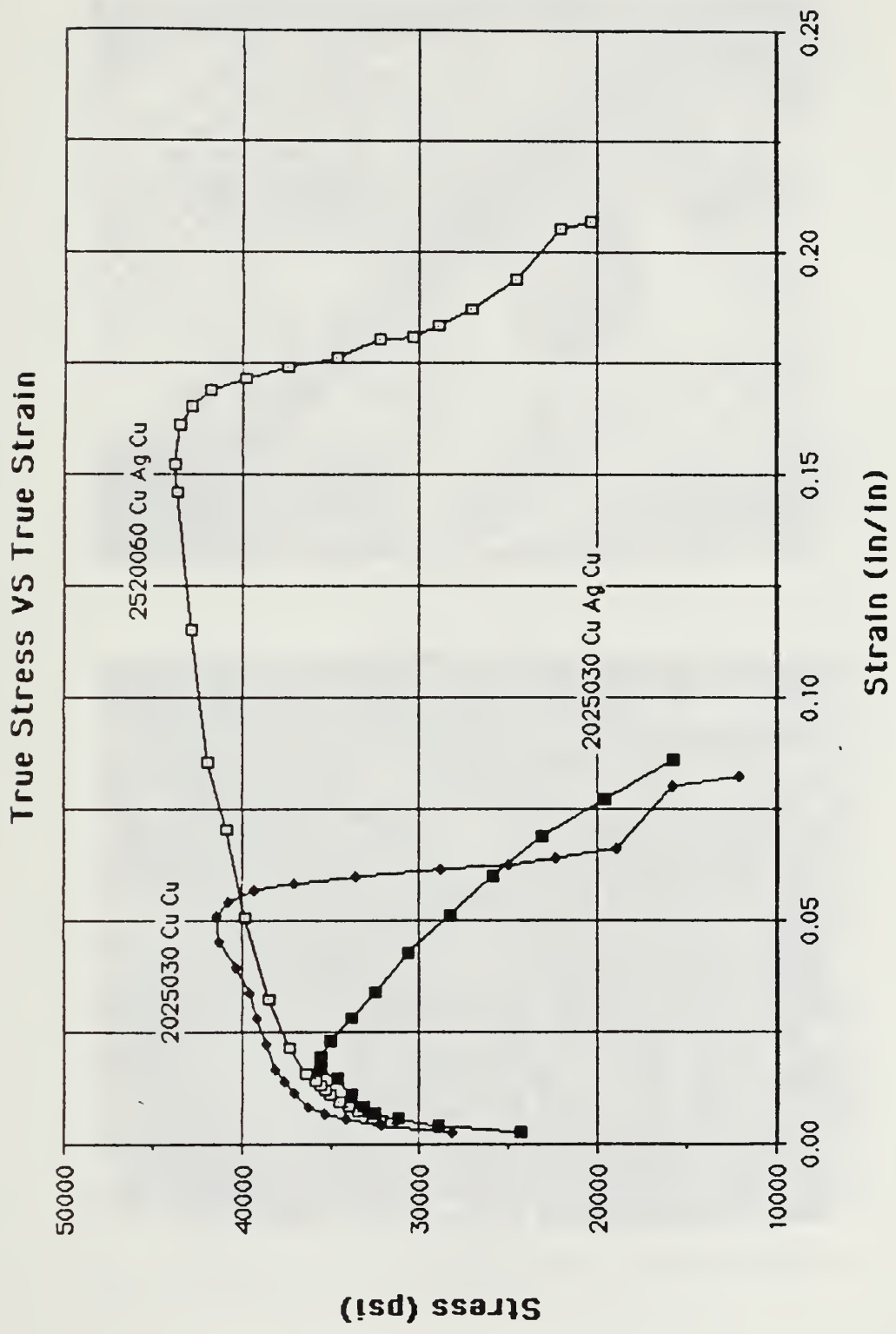


Figure 7  
True Stress VS True Strain for Tensile Specimens Which Plastically Deformed

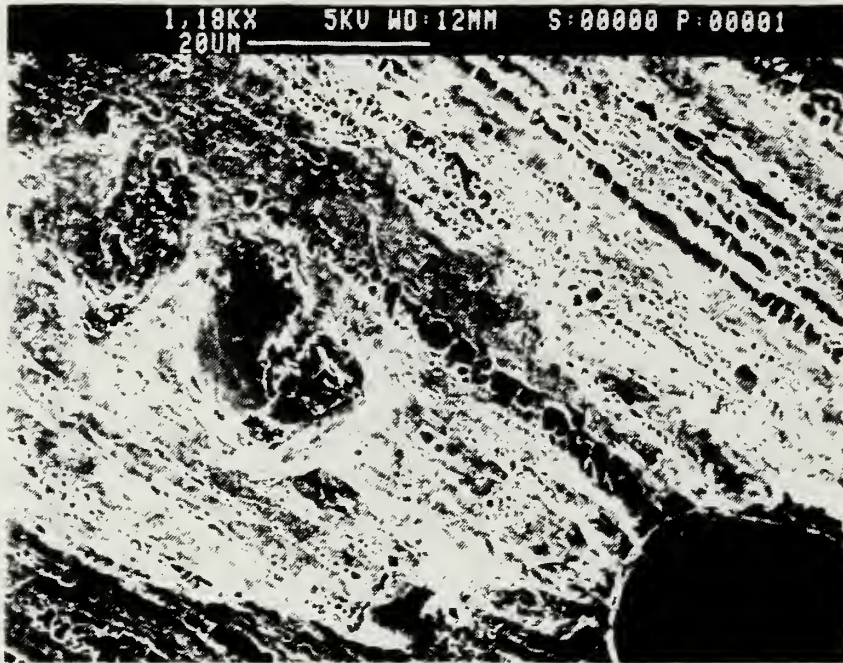


Figure 8  
Silver Failure Surface On Cu-Ag-Cu Tensile Bond  
25-200-60

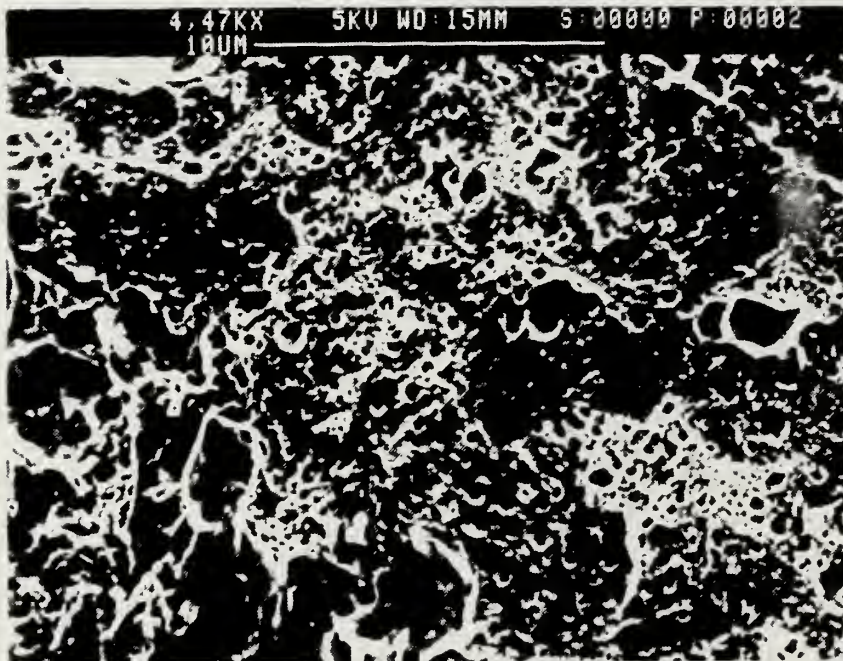


Figure 9  
Copper Fracture Surface On Cu-Cu Tensile Bond  
20-250-30



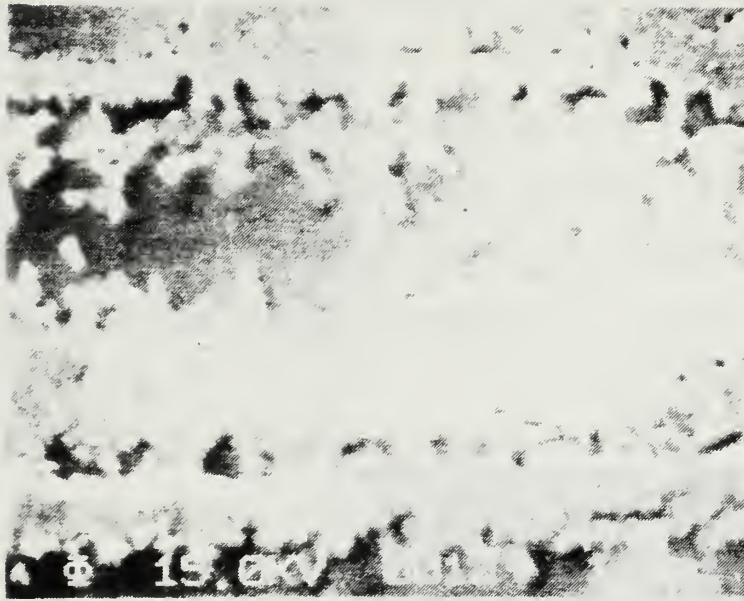


Figure 10  
Silver Failure Surface On Cu-Ag-Cu Foil Bond  
20-250-30

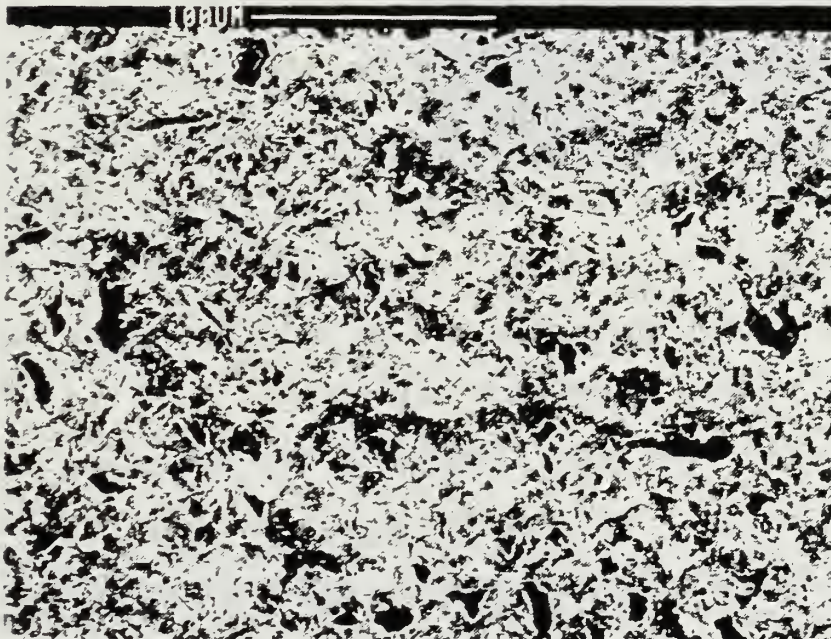


Figure 11  
Failure Surface On Cu-Cu Tensile Bond  
20-250-30

always occurred at silver-copper interfaces. The fracture path for the copper-copper tensile specimen follows the interface (Figure 11). This is indicated by regions where bonding has not occurred which in some cases still show scratches from the polishing process used prior to bonding. It is likely that these unbonded regions act as stress concentrators during tensile testing and promote fracture along the interface.

Copper-silver-copper foil bond specimens have been peeled apart and elemental analysis performed by Auger spectroscopy. Auger maps indicate that copper is found on the entire silver bond surface and silver on the copper bond surface (Figures 12,13). Light regions indicate the presence of the element being mapped. The strength of the Auger signal is indicated by the intensity or brightness of the pixel. The maps suggest that bonding occurred over the entire mating surface but not sufficiently to produce 100 percent ductile failure. Groove replication from the silver to foil copper indicates the extent of plastic deformation and the extent of surface contact.

Chlorine was also present at the interface as indicated in Figure 14. Chlorine coverage is estimated at less than one monolayer based on the valence electron Auger peak intensity for silver relative to core level transition intensities. The low energy valence transitions have a much shallower escape depth than the core transitions and are



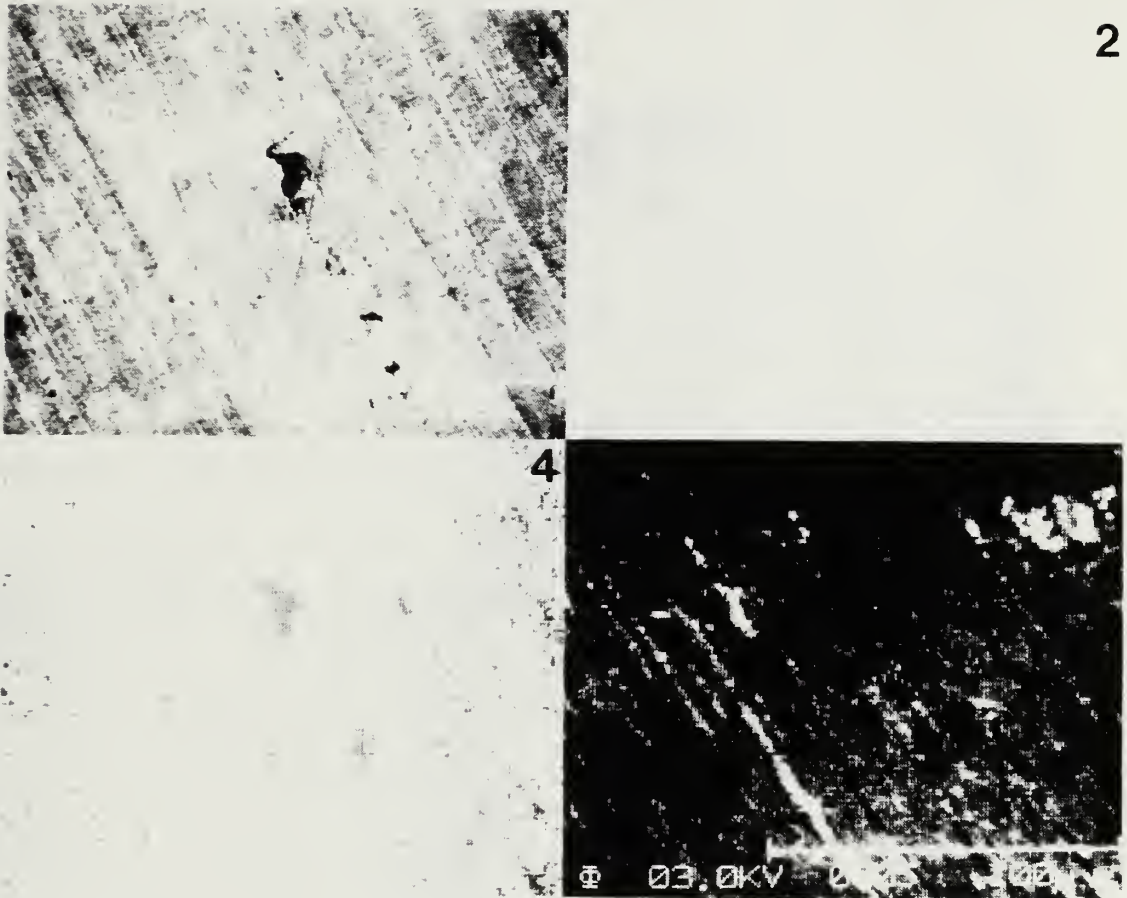
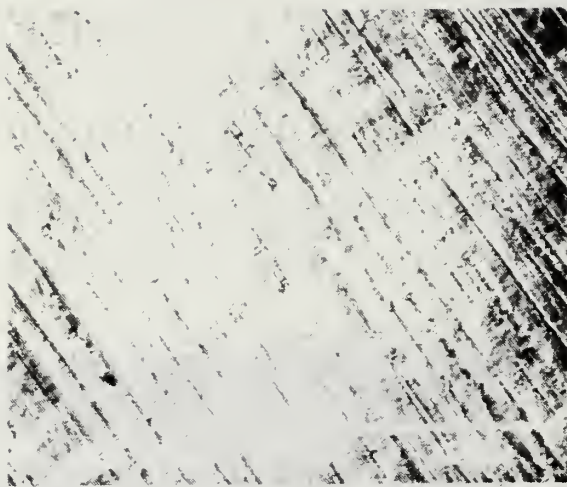


Figure 12  
Electron Micrograph And Elemental Auger Maps Of  
Copper Foil Peel Surface: 20-150-30  
Clockwise from upper left: (1)secondary electron image,  
(2)copper map, (3)silver map, (4) sulfur map.



2

4

3

Figure 13  
Electron Micrograph and Elemental Auger Maps Of  
Silver Foil Peel Surface: 20-150-30  
Clockwise from upper left: (1)secondary electron image,  
(2)silver map, (3)copper map, (4)chlorine map.

charge region like a parallel plate capacitor charged to a potential equivalent to the work function divided by the charge of an electron, suggests that one electron is transferred for every 1000 atoms at the surface. This number is small enough to put such an effect beyond the range of detection for the current spectrometer.

Energy dispersive X-ray analysis conducted on fracture surfaces of Cu-Ag-Cu tensile test specimens, like the one shown in Figure 15, confirmed the visual evidence that failure occurs along the copper-silver interface. It can be seen from the micrograph (Figure 15) that the failure surface moves from one interface to the other across the diameter of the sample.

Auger depth profiling was difficult for the Cu-Cu and CU-Ag-Cu foils examined. Surface roughening was a major problem in attempting to profile from silver to copper. When profiled from the copper to silver the depth profiles did show (Figure 16) that carbon is diffusing away from the interface into the copper. The high level of carbon observed near the interface is believed to be real but it is not possible at this time to explain the origin of such a large signal. This diffusion process can make it easier for the atoms at the surface to get close enough to form bonds across the interface. Similar data for silver is not available because of a peak over lap between carbon and one of the lower energy core level peaks for silver. It may be

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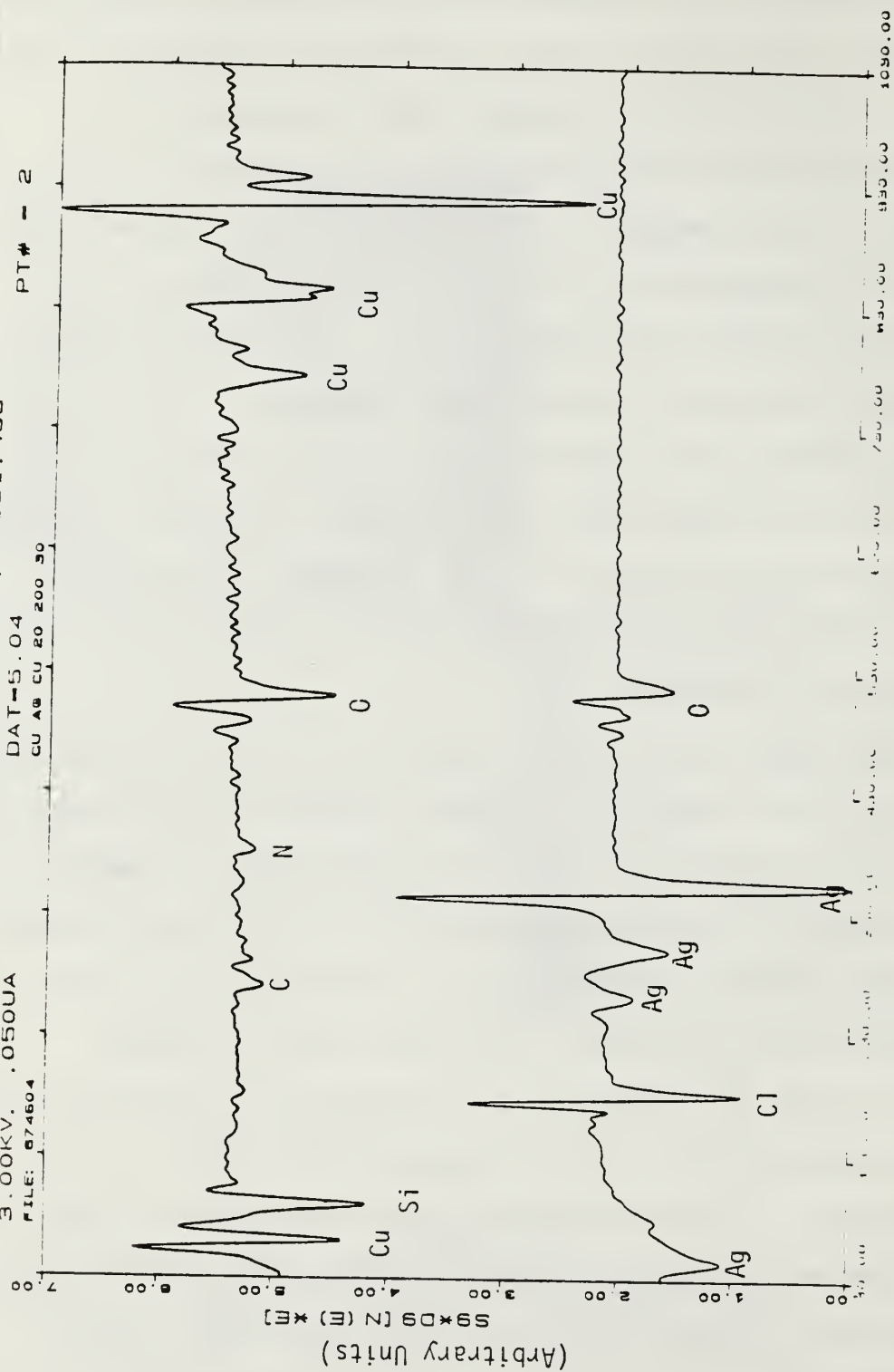


Figure 14  
Auger Spectra From Peeled Foil Samples: 20-200-30

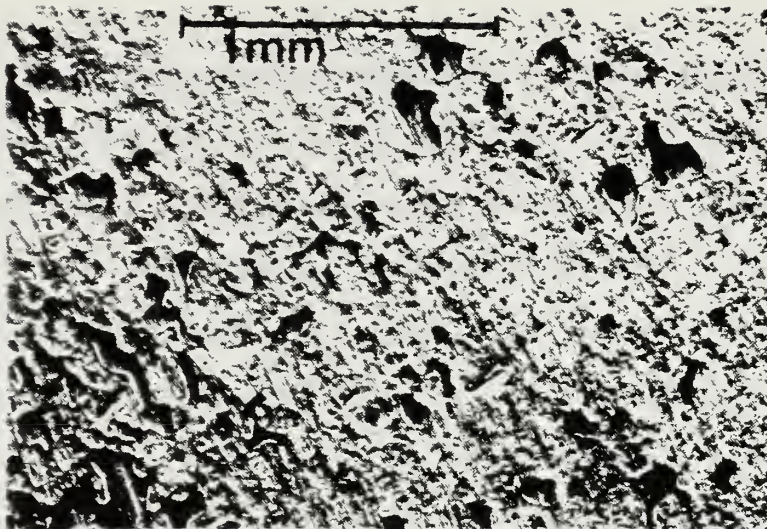


Figure 15  
Secondary Electron Image of Cu-Ag-Cu Tensile Specimen  
Failure Surface: 20-150-30

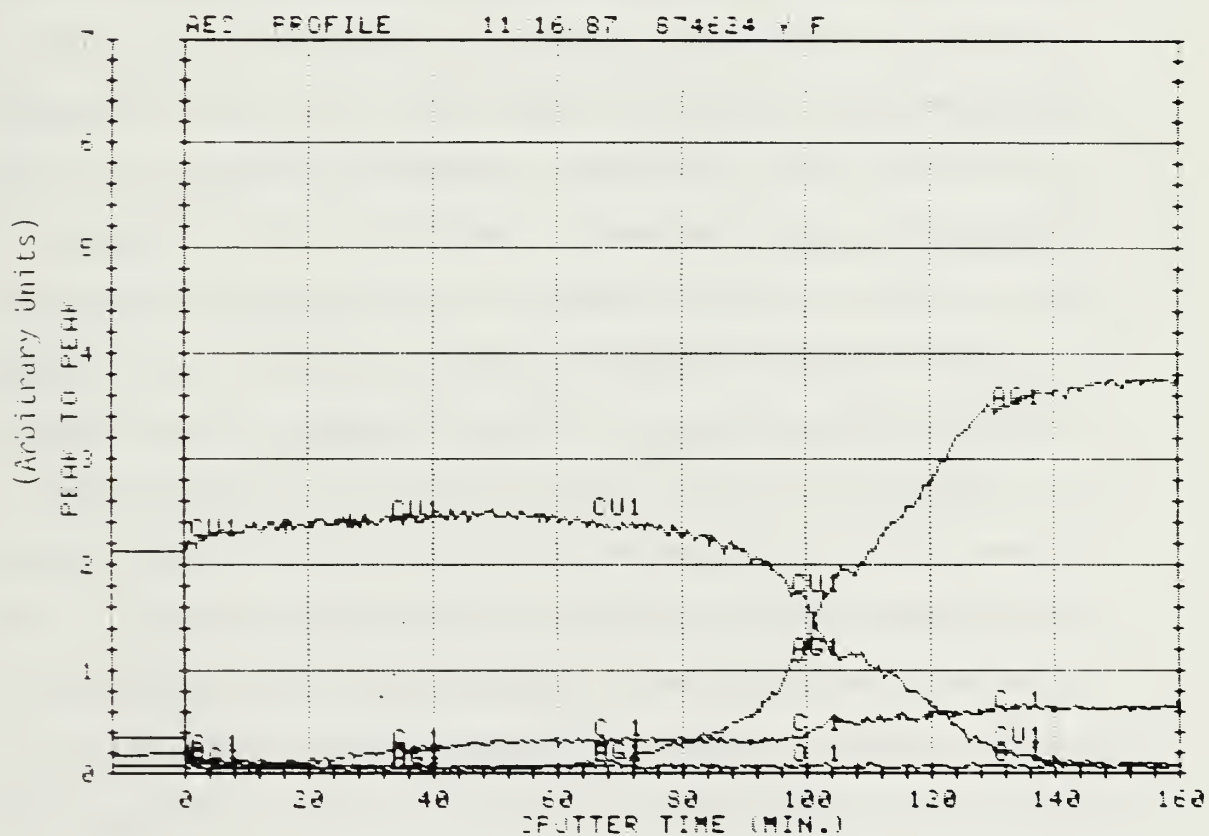


Figure 16  
Auger Depth Profile for Sample 20-150-30



easily attenuated by surface contaminants. The amplitude of the valence Auger peak relative to core peaks can thus serve as a gauge for surface layer coverage. Chlorine was not detected at the interface in any of those depth profiles for which this element was monitored. It is possible that chlorine is missed at the interface due to surface roughening during profiling.

Efforts were made to determine if charge transfer associated with metallic bonding could be observed in the Cu-Ag-Cu system. The difference in work functions (4.73 eV for silver, 4.46 eV for copper) indicates electrons would be transferred from copper to silver. If this charge transfer is limited to the 4s electron of copper one should be able to monitor the relative peak intensities for the valence transitions across the interface. It is expected that the 47 eV peak for silver would be enhanced and the 60 eV peak for copper reduced relative to their respective core level peaks. High resolution spectra taken from 15 to 1015 eV indicate that the valence to core level peak to peak ratios do not deviate from bulk values for the pure metals.

The inability to see a change in amplitude may be due for two reasons. First, s electrons are not the only electrons participating in the metallic bond. In silver and copper the underlying d electrons also take part. Second, a very simplistic calculation, which treats the interface

assumed that the profile for carbon in silver is similar to that observed for copper. Carbon diffuses interstitially in both metals and may actually diffuse faster in silver due to the larger lattice spacing. The diffusivity of carbon in copper and silver could not be found to confirm this assumption.

Depth profiles failed to detect oxygen at the interface as has been seen by other investigators for different systems than those investigated here [Ref. 21]. It is assumed that oxygen has also diffused away from the interface and is there only in quantities too small to be detected. This is a reasonable assumption because Munir [Ref. 22] presents data which indicate silver oxide decomposes at about 150C and, given sufficient diffusivity, dissolve into the silver and copper matrices. The dissolution time for a 100 angstrom thick oxide film on copper is a few seconds at 250C, a few hundred seconds at 200C and about  $10^5$  seconds at 150C. These results help explain why bonds at the lower temperatures (150C) were so weak. The steep exponential nature of oxide dissolution time for the 100 angstrom thick layer on copper also sets a threshold temperature, alluded to earlier, somewhere between 150C and 200C.

## V. SUMMARY AND CONCLUSIONS

Auger depth profile data indicate that contaminants normally found at the interface of samples bonded in air are not confined to the interface after bonding. The depth profiles show that carbon is diffusing away from the interface and oxygen is no longer present there in sufficient quantities for detection after successful bonding. The oxide of silver decomposes to oxygen and pure silver above about 150C and copper can dissolve its oxide during the times used for bonding (provided no additional oxygen reaches the bond interface) at temperatures equal to or greater than about 200C [Ref. 22]. The data presented for the copper oxide [Ref. 22] supports the suggestion that the threshold temperature for solid state bonding observed in this work can be related directly to the temperature at which the surface oxide of copper dissolves in a reasonable amount of time. There is no evidence that chemically active species such as chlorine are removed in a similar manner. This self cleaning effect is probably the main reason it was possible to bond the test specimens in an ambient atmospheric environment at such low temperatures.

It is not possible for silver or copper to dissolve a tenacious (high negative heat of formation) oxide layer associated with some elements, chromium and aluminum for

example. In these cases it would be desirable to put down a scavenging film which has a larger negative heat of formation for its oxide and then cover this layer with silver or copper for subsequent bonding. Chromium on stainless steel covered by silver or copper should be investigated as a means of overcoming interlayer adherence problems which have been observed for this system.

Evidence is presented supporting extensive metal metal contact for the range of bond parameters studied. It has also been observed that the failure mode is not 100 percent ductile except for the copper-copper bond at 250C, 20ksi due to interface weaknesses. The fractional amount of ductile fracture observed appears to be a function of temperature and pressure, the maximum amount occurring at elevated temperatures and pressures. All fracture surfaces contained features which indicate bonding did not occur over the total cross sectional area of the joint. These regions of poor or no bonding can act as local stress concentrators and are oriented perpendicular to the stress during testing so that they produce a maximum stress concentrating effect during tensile loading. It is possible that these stress risers are responsible for driving the failure path along the interface in all cases examined.

The relative strength of the Cu-Cu bond versus the Cu-Ag-Cu bond can be related to the addition of a positive interface energy term in the dissimilar metal joint which

reduces the joint efficiency. It would be possible to evaluate this positive energy term by calculating the difference in areas under the stress strain curves if ideal bonds were formed. Assuming the true area of contact is the same for similar bond parameters, the data presented here suggests that the chemical interface energy term is small and greater than zero as indicated by the slight degradation of mechanical properties for the Cu-Ag-Cu system with respect to the Cu-Cu system. This agrees with the analysis of Oberg, et al., [Ref. 15] which predicts a small positive chemical energy term for the Cu-Ag interface.

There is less data explaining the improved bond characteristics observed at higher bond pressures. Auger analysis of peeled interface surfaces does not indicate any significant change in the surface composition of foils at 25ksi and foils at 20ksi. It is assumed that higher bond pressures increase the true contact area and in this manner enhances the bond performance. Additional work in this area would examine bonding pressures from 20ksi to 60ksi at 200C. Bond tests at higher loads will have to be conducted under hydrostatic pressure to avoid deformation of the tensile specimen. At 20ksi the tensile yield strength of the silver has been exceeded by about an order of magnitude while the yield strength of the copper may not have yet been achieved. It is possible that the silver strain hardened and ceased to



flow plastically. The effect of higher strength/toughness at higher bond pressure may be due to the onset of plastic flow in the copper foil.

ESCA (Electron Spectroscopy for Chemical Analysis) is another surface analytical tool which might shed some light on the charge transfer expected in dissimilar metal bonding. The advantage of this technique is that the electrons are ejected directly from the atom through interaction with high energy X-rays. The electrons analyzed come primarily from ground state atoms which are not affected by the vacant inner core relaxation associated with Auger analysis. Sensitivity levels for both analyzers are about the same but ESCA peaks are more easily deconvoluted and an accurate measurement of the area under the curve may more readily indicate the charge transfer predicted theoretically.

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